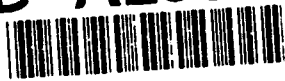


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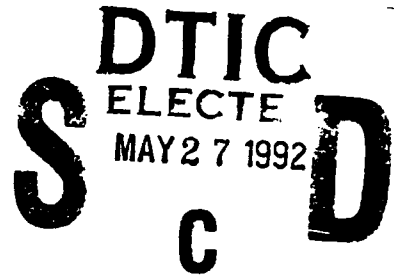


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Near-IR Absorption Spectra for the Buckminsterfullerene Anions:  
An Experimental and Theoretical Study

by

D. R. Lawson, D. L. Feldheim, C. A. Foss, P. K. Dorhout, C. M.  
Elliott, B. A. Parkinson and C. R. Martin

Department of Chemistry  
Colorado State University  
Ft. Collins, CO 80523

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Del R. Lawson, Daniel L. Feldheim, Colby A. Foss,  
Peter K. Dorhout,\* C. Michael Elliott,\* Charles R. Martin,\*  
Bruce A. Parkinson\*

Department of Chemistry  
Colorado State University  
Fort Collins, CO 80523

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### Abstract

$C_{60}$  can exist in a number of oxidation states including  $C_{60}^{1-}$ ,  $C_{60}^{2-}$  and  $C_{60}^{3-}$ . Ultraviolet-visible absorption data have been described for  $C_{60}$ ,  $C_{60}^{1-}$  and  $C_{60}^{2-}$ . Near-infrared absorption data have not been presented for any of the oxidation states of  $C_{60}$ . We have discovered that this is a serious oversight, because near-IR absorption peaks which are unique to  $C_{60}^{1-}$ ,  $C_{60}^{2-}$  and  $C_{60}^{3-}$  are observed upon one, two and three electron electrochemical reductions of  $C_{60}$ . We have rationalized the energies and intensities of these electronic absorptions based on modifications of the known molecular orbital diagram for  $C_{60}$ . The near-IR absorptions reported here should provide a clear and unambiguous route for determining the oxidation state of  $C_{60}$  in solution.

$C_{60}$  can exist in a number of oxidation states including  $C_{60}^{1-}$ ,  $C_{60}^{2-}$  and  $C_{60}^{3-}$  (1-4). UV-visible absorption data have been described for  $C_{60}$  (4-8),  $C_{60}^{1-}$  and  $C_{60}^{2-}$  (2). Near-infrared absorption data have not been presented for any of the oxidation states of  $C_{60}$ . We have discovered that this is a serious oversight, because near-IR absorption peaks which are **unique to  $C_{60}^{1-}$ ,  $C_{60}^{2-}$  and  $C_{60}^{3-}$**  are observed upon one, two and three electron electrochemical reductions of  $C_{60}$ . We have rationalized the energies and intensities of these electronic absorptions based on modifications of the known molecular orbital diagram for  $C_{60}$  (9-12). The results of these experimental and theoretical analyses are reported in this correspondence.

Fullerene "soot" was obtained from Texas Fullerenes. Pure  $C_{60}$  and  $C_{70}$  were isolated from this soot as per Ajie, et al. (8).  $C_{60}$  solutions (0.15 mM) were prepared in benzonitrile which was 0.1M in  $Bu_4NPF_6$  (supporting electrolyte) (13). Spectra for the various  $C_{60}$  species were obtained by mounting an optically-transparent thin-layer electrochemical cell (14,15) within the sample chamber of a Hitachi 3501 near-IR-UV-visible spectrometer. A spectrum of  $C_{60}$  was first obtained with the cell at open circuit. Cyclic voltammetric experiments were then run to determine the potentials required to quantitatively reduce  $C_{60}$  to the mono, di and trivalent anion. These voltammograms were essentially identical to those presented in the literature (1,2). Potentials of -1.1 V, -1.6 V and -2.2 V vs.  $Ag/Ag^+$  (15) were used to generate the  $C_{60}^{1-}$ ,  $C_{60}^{2-}$  and  $C_{60}^{3-}$ , respectively.

As has been observed previously (2),  $C_{60}$  (Figure 1, curve A) shows absorptions at 330 nm (strong), 410 nm (weak) and 550 nm (weak and broad). The near-IR region for  $C_{60}$  is, however, featureless. In contrast, **all of the  $C_{60}$  anions show unique signatures in the near-IR** (Figure 1). The positions of and molar absorptivities for these previously-unreported near-IR transitions are presented in Table I.

A portion of the molecular orbital diagram (9,10) for the icosahedral ( $I_h$ )  $C_{60}$  molecule is shown in Figure 2A. The HOMO is the completely-filled  $h_u$  orbital and the LUMO is the  $t_{1u}$  orbital. The first transition, assigned to the band at 550 nm (dashed line,  $v$ , in Figure 2A), is symmetry-forbidden in  $I_h$ . Furthermore, since the ground state of  $C_{60}$  is

$A_{1g}$  (i.e. spherical), the  $h_u \rightarrow t_{1u}$  transition corresponds to a  $\Delta l$  that is not equal to  $\pm 1$ . This transition is observed, however, because of vibronic coupling (9) to the totally-symmetric  $H_g$  vibration (Raman-active band at  $770\text{ cm}^{-1}$ ) (16,17).

Placing an electron into the  $t_{1u}$  LUMO (to generate  $C_{60}^{1-}$ ) should result in a new, symmetry-allowed,  $t_{1u} \times T_{1u} \times t_{1g}$  transition (9) near 1.1 eV ( $T_{1u}$  is the electric dipole moment operator in  $I_h$ ). It is unlikely, however, that this electron would occupy a triply degenerate "ground state" without experiencing some type of Jahn-Teller distortion. Such distortion is predicted for the  $C_{12}$  and  $C_{20}$  species with degenerate ground states (11) and is supported by ESR measurements on  $C_{60}^{1-}$  (2,18,19). All of this is consistent with a symmetry reduction that lowers the energy of the electron in  $t_{1u}$ .

A distortion to cubic symmetry, consistent with the fcc crystal structure of solid  $C_{60}$  (20), does not reduce the symmetry of the  $t_{1u}$  orbital. In contrast, reduction to hexagonal  $D_{6h}$  symmetry (21), while retaining the center of symmetry, does permit a transition from the  $a_{2u}$  to  $e_{1g}$  orbitals (Figure 2B,  $a_{2u} \times E_{1u} \times e_{1g}$ ). We propose that this transition accounts for the 1078 nm (1.15 eV) peak for  $C_{60}^{1-}$ . The high energy vibronic manifold (800 to 1000 nm) is presumably due to vibronic transitions to the  $a_{2g}$  level. This loss of symmetry and lowering of the  $a_{1u}$  orbital should also shift the visible " $h_u \rightarrow t_{1u}$ " transition to lower energies ( $v$  in Figure 2B); this shift is observed in the  $C_{60}^{1-}$  spectrum. The broadening and shifting of the 330 nm transition (2) can also be accounted for by this diminution in symmetry.

When  $C_{60}^{1-}$  is reduced to the dianion the electrons occupy the two  $e_{1u}$  orbitals rather than paying the energetic price of pairing in the  $a_{2u}$  orbital (Figure 2C). This picture is consistent with the ESR spectrum reported for this  $S = 1$  system (2). As indicated in Figure 2C, this should result in two allowed transitions,  $e_{1u} \times A_{2u} \times e_{1g}$  and  $e_{1u} \times E_{1u} \times a_{2g}$ . These transitions should occur at ca 1.3 and 1.5 eV. We propose that these transitions are responsible for the 952 nm (1.3 eV) and 810 nm (1.5 eV) peaks in the  $C_{60}^{2-}$  spectrum. Furthermore, as was seen in the  $C_{60}^{1-}$  case, the " $h_u \rightarrow t_{1u}$ " transition is again shifted to

lower energy, consistent with a lowering in energy of the formerly  $t_{1u}$  orbital to accommodate the two unpaired electrons in the  $e_{1u}$  orbitals.

The  $C_{60}^{3-}$  spectrum is particularly interesting. If  $C_{60}^{3-}$  is  $S = 3/2$ , there is no reason for a distortion from  $I_h$  symmetry, and the electrons should be found in the triply-degenerate  $t_{1u}$  orbital (symmetric ground state). We would, therefore, expect to see a single, sharp transition near 1.1 eV. In contrast, we observe at least three distinct absorptions in the near-IR. Furthermore, while the ESR spectrum is not conclusive,  $C_{60}^{3-}$  seems to resemble an  $S = 1/2$  system (22). Based on these observations, two molecular orbital scenarios can be proposed for  $C_{60}^{3-}$  in  $D_{6h}$ :  $(a_{2u})^2(e_{1u})^1$  or  $(e_{1u})^3(a_{2u})^0$ . In both of these examples, a degenerate ground state is realized, and we would expect a further reduction in symmetry to remove this degeneracy. One possibility is  $D_{2h}$  symmetry, illustrated by the molecular orbital diagram shown in Figure 2D. The allowed transitions from this  $(b_{1u})^2(b_{2u})^1(b_{3u})^0$  ground state configuration would be  $b_{1u} \rightarrow b_{2g}$ ,  $b_{2u} \rightarrow b_{1g}$ ,  $b_{1u} \rightarrow b_{3g}$ , and  $b_{2u} \rightarrow b_{3g}$ , in order of decreasing energy. It is not too surprising that four clearly-resolved peaks are not observed in the near-IR spectrum of  $C_{60}^{3-}$  (Figure 1, curve D) because of the broadening of these transitions due to the lowering of symmetry and the increasing number of available vibrational manifolds. This undoubtedly accounts for the complex features of this spectrum.

The near-IR absorptions reported here should provide a clear and unambiguous route for determining the oxidation state of  $C_{60}$  in solution. Raman studies of the reduced  $C_{60}^{n-}$  species should corroborate the discussions presented here. Furthermore, it is worth mentioning that we have observed analogous absorptions for the anions of  $C_{70}$  (23).

### Acknowledgements

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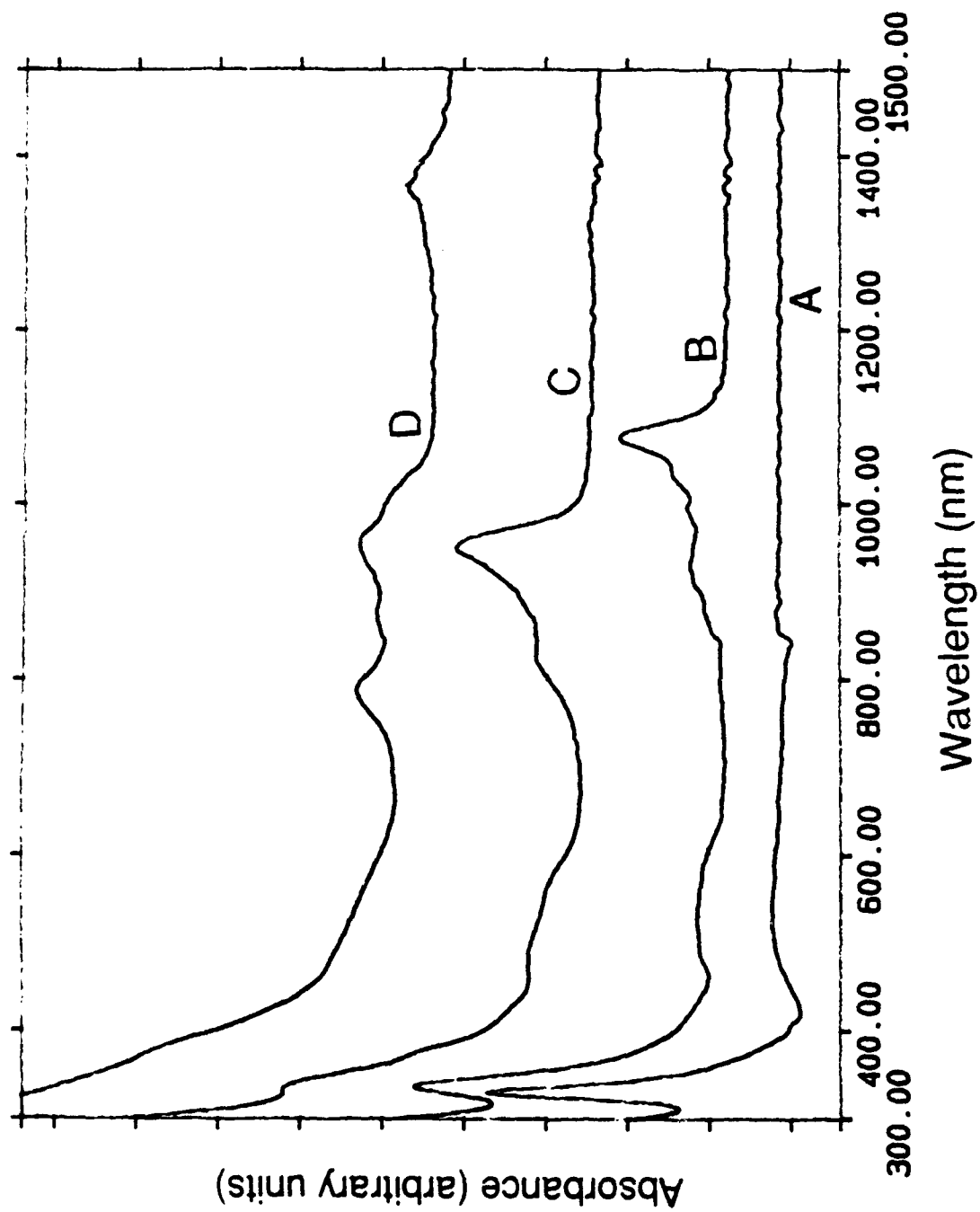
Table I. Spectral data for the various C<sub>60</sub> species.

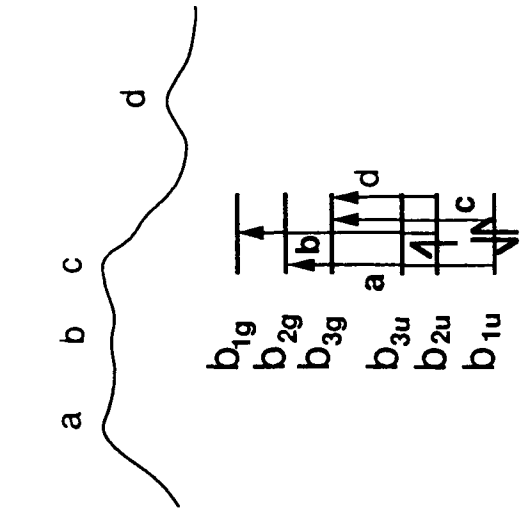
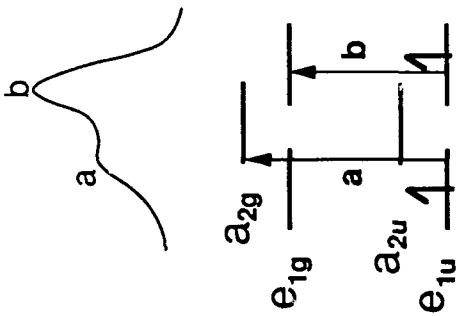
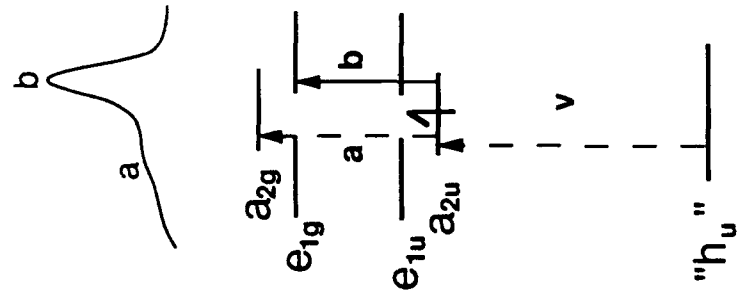
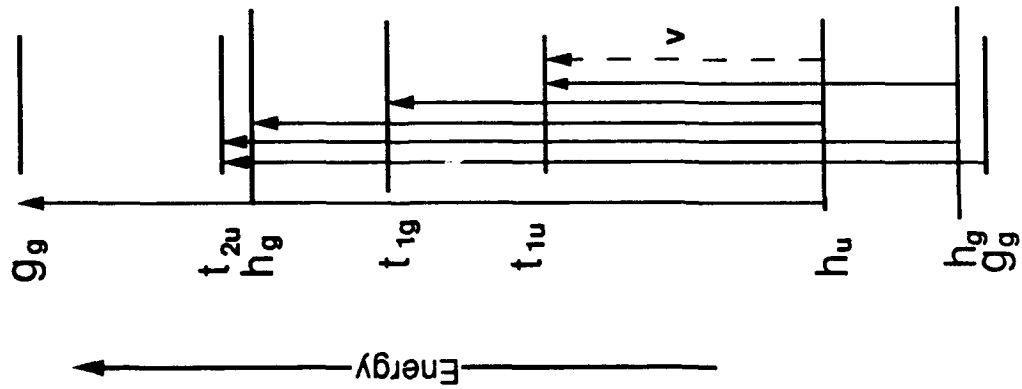
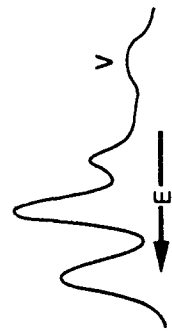
Species	$\lambda$ max (nm)	Extinction Coefficient (L/M•cm)
C <sub>60</sub>	330	48,000
C <sub>60</sub> <sup>-1</sup>	1078	19,000
C <sub>60</sub> <sup>-2</sup>	952	24,000
	810	7,000
C <sub>60</sub> <sup>-3</sup>	1378	10,000
	956	16,000
	788	19,000

## Figure Captions

Figure 1. UV-visible-near-IR absorption spectra for (A)  $C_{60}$ , (B)  $C_{60}^{1-}$ , (C)  $C_{60}^{2-}$ , and (D)  $C_{60}^{3-}$ . A blank sample of the supporting electrolyte solution was used for background subtraction. The feature at  $\sim 840$  nm corresponds to an instrument grating change.

Figure 2. (A) Molecular orbital diagram for  $C_{60}$  (9-12). Proposed molecular orbital diagrams for (B)  $C_{60}^{1-}$ , (C)  $C_{60}^{2-}$ , and (D)  $C_{60}^{3-}$ . The transitions in B-D are labelled and are assigned to the simulated near-IR spectra above each example.





D

C

B

A